



Modeling of the cranking and charging processes of conventional valve regulated lead acid (VRLA) batteries in micro-hybrid applications



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HIGHLIGHTS

- The stop–start cycling of a conventional VRLA battery was modeled.
- The effect of stop–start cycling on electrode sulfation aging was analyzed.
- Cranking pulses produce high overpotentials at the negative/separator interface.
- Parametric studies were done to analyze their effects on sulfation over cycling.

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ABSTRACT

The cranking and charging processes of a VRLA battery during stop–start cycling in micro-hybrid applications were simulated by one dimensional mathematical modeling, to study the formation and distribution of lead sulfate across the cell and analyze the resulting effect on battery aging. The battery focused on in this study represents a conventional VRLA battery without any carbon additives in the electrodes or carbon-based electrodes. The modeling results were validated against experimental data and used to analyze the “sulfation” of negative electrodes – the common failure mode of lead acid batteries under high-rate partial state of charge (HRPSoC) cycling. The analyses were based on two aging mechanisms proposed in previous studies and the predictions showed consistency with the previous teardown observations that the sulfate formed at the negative interface is more difficult to be converted back than anywhere else in the electrodes. The impact of cranking pulses during stop–start cycling on current density and the corresponding sulfate layer production was estimated. The effects of some critical design parameters on sulfate formation, distribution and aging over cycling were investigated, which provided guidelines for developing models and designing of VRLA batteries in micro-hybrid applications.

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1. Introduction

The U.S. Environmental Protection Agency (EPA) and National Highway Traffic Safety Administration (NHTSA) recently announced a joint final rulemaking on standards to reduce greenhouse gases and to improve fuel economy for light-duty vehicles in the United States for model years 2017–2025. The final standards are projected to reduce carbon dioxide emissions from 250 g mile^{−1} in 2016 to 163 g mile^{−1} in model year 2025, which is equivalent to improving

the fleet average fuel economy from 35.5 miles gallon^{−1} to 54.5 miles gallon^{−1}. As the regulation becomes more and more stringent, the auto industry will employ every technology available to meet these standards. Micro-hybrid vehicles with “stop–start” and “regenerative braking” features are a potential solution under intense development today. Lead acid batteries in such applications experience extended discharging, high-rate cranking and follow-on charging processes more frequently than those used in conventional vehicles without “stop start”. Under such high-rate partial state of charge (HRPSoC) operations, negative electrode sulfation is always considered as the major failure mode of batteries [1–3]. Presently two major mechanisms of sulfation formation have been proposed and accepted, which constitute the basis of our analyses in this paper.

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The first one was from Lam et al. [2], who identified high-rate discharge as the key factor responsible for the build-up of lead-sulfate layers in negative electrodes after a teardown analysis of batteries operated under HRPSoc duties. It was shown that a compact layer of sulfate was left on the surface of the negative electrode in a cell after charging, which means hard sulfation at the negative electrode was caused by the quick precipitation of Pb^{2+} during the high-rate discharge process. In our study, this process is referred to as the quick-precipitation mechanism. The second mechanism was developed by Yamaguchi et al. [4], who observed the formation of larger sulfate particles with flatter surfaces after the battery has been dormant for a long time under incomplete charge. This was explained by the sulfate re-crystallization mechanism, which was verified by experimental results in other studies [5,6].

With knowledge of these two mechanisms, one can anticipate that in stop–start cycling, frequent high-rate discharge may lead to the accumulation of a hard sulfation layer at the negative electrodes; Also, the short charge intervals between stop–start events can leave batteries incompletely charged, where small sulfate particles would re-crystallize into hard particles that are difficult to be converted back. Although there are current development proposed to accommodate the HRPSoc duties by using carbon additives or by using new carbon-based electrodes [7], this paper focuses on the conventional VRLA batteries without any carbon additives or carbon-based electrodes. The modeling approach should be adjusted if carbon additives or carbon-based electrodes are considered, which can be conducted in our future studies.

Presently, physico-chemical modeling of the above-mentioned two aging processes based on fundamental laws is very limited. Thele et al. [8] developed an impedance-based battery model with “hardening crystals” aging mechanism (same concept as the re-crystallization mechanism) integrated, wherein the modeling results showed improvement of SOC prediction compared to those without consideration of crystal hardening effect. The “hardening crystals” modeling approach was also extended to explain and predict the limit of charge acceptance during charging processes in their later work [9]. However, all of their work was based on electric equivalent circuit models and thus the crystal hardening effect was represented by a resistor in parallel with a capacitor, which did not fundamentally model the physical process, and consequently was incapable of predicting the details (e.g. spatial distribution or easiest locations) of crystal hardening across the battery electrodes.

The objective of this paper is three-fold: 1) To understand the internal physical process of the formation and distribution of lead sulfate that affects both the aging process inside a conventional VRLA battery during frequent cranking and follow-up charging through computer modeling; 2) To quantitatively estimate the effect of high-rate cranking pulses on lead sulfate formation and accumulation on electrodes; and 3) To study the effects of critical design parameters on lead-sulfate distribution and consequential sulfation accumulation, providing guidelines of battery design and development for micro-hybrid applications.

2. Mathematical model

The mathematical model used in this study was originally developed by Wang et al. [10–12] and integrated with electric double layer effect in their follow-up work [13]. This model was developed from first-principle conservation laws, such as charge, mass and species conservations. This model, therefore, is intrinsically capable of revealing the details of internal physical and chemical processes inside lead acid batteries during charge and discharge. In our study, this model has been simplified by removing gassing side reactions and thermal evolution. This is because the

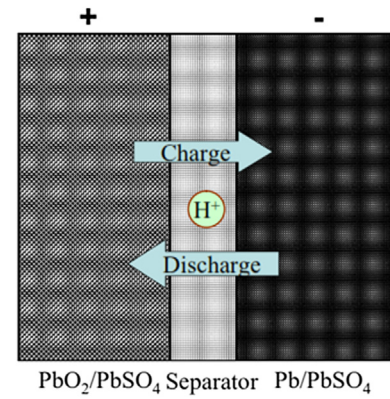


Fig. 1. Schematic of a VRLA cell.

voltage limit of our charging system on board is usually 14.3 V/6 cells, which we believe does not trigger much gassing reactions; also, all of our simulation focus on the transient processes and thus the temperature variation would not be pronounced enough to affect the results. Therefore it would not be worthwhile to add complexity without seeing significant impact on the results. Inheriting from the original work, the model itself is a performance model and does not mathematically model the hard sulfation process, but the simulation results generated in this study are analyzed based on the two aging mechanisms proposed and validated by other studies [1,4–6], providing the details of physical processes inside the battery to help better understand and prevent battery sulfation aging in stop–start applications.

A schematic of the VRLA cell, shown in Fig. 1, displays the cell region modeled. The battery modeled here is a conventional VRLA battery, thus the cell only comprises of conventional sponge lead dioxide and lead paste without any carbon additives as the electrodes and absorbent glass mat as the separator. Electrolyte is stored and stabilized in the separator. The Pb alloy grids work as the current collectors for both electrodes.

All the model governing equations are summarized in Table 1. The physical meaning of all modeling parameters can be found in Table 2. The battery specifications are listed in Table 3. The definitions of coefficients and source terms related to the positive

Table 1
Summary of governing equations.

Kinetic rate equations	$i = i_{0,\text{ref}} \left(\frac{C^{\text{H}}}{C^{\text{H}}_{\text{ref}}} \right)^{\gamma} \left[\exp \left(\frac{\alpha_a F}{RT} \eta \right) - \exp \left(- \frac{\alpha_c F}{RT} \eta \right) \right] \quad (1)$
Conservation of charge	$\nabla \cdot (\kappa^{\text{eff}} \nabla \phi_e) + \nabla \cdot [\kappa_D^{\text{eff}} \nabla (\ln C^{\text{H}})] = -ai - aC_{\text{dl}} \frac{\partial(\phi_s - \phi_e)}{\partial t} \quad (2)$
	$\nabla \cdot (\sigma^{\text{eff}} \nabla \phi_s) = ai + aC_{\text{dl}} \frac{\partial(\phi_s - \phi_e)}{\partial t} \quad (3)$
Conservation of mass	$\frac{\partial \epsilon_e}{\partial t} = S_e^{\text{V}} \quad (4)$
	$\frac{\partial \epsilon_s}{\partial t} = S_s^{\text{V}} \quad (5)$
Conservation of species	$\frac{\partial(\epsilon_e C^{\text{H}})}{\partial t} = \nabla \cdot (D_{\text{eff}}^{\text{H}} \nabla C^{\text{H}}) + S^{\text{H}} \quad (6)$

Table 2
Explanation for modeling parameters.

a	Specific surface area ($\text{cm}^2 \text{cm}^{-3}$)
C^H	Acid concentration (mol m^{-3})
C_{ref}^H	Reference acid concentration (mol m^{-3})
C_{dl}	Capacitance of double layer effect (Farad cm^{-2})
D_{eff}^H	Effective diffusivity ($\text{m}^2 \text{s}^{-1}$)
F	Faraday constant (Coulomb mol^{-1})
i	Transfer current density (A cm^{-3})
i_0	Exchange current density (A cm^{-3})
R	Universal gas constant ($8.3143 \text{ J (mol}^\circ\text{K)}^{-1}$)
S	Source term
T	Absolute temperature ($^\circ\text{K}$)
ΔU	Equilibrium potential (V)
Greek letters	
α_a	Anodic transfer coefficient
α_c	Cathodic transfer coefficient
ϵ	Volume fraction
η	Overpotential (V)
κ	Electrolyte conductivity (Siemens m^{-1})
σ	Conductivity of solid phase (Siemens m^{-1})
φ	Potential (V)
γ	Dependency index
Superscript	
H	Hydrogen ion
Subscripts	
dl	Double layer effect
D	Diffusion
e	Electrolyte phase
eff	Effective quantity
ref	Reference quantity
s	Solid phase
V	Volume

electrode, separator and negative electrode used in this study are the same as those in the original modeling work [9,10], which will not be detailed here. The governing equations are discretized based on finite volume method and solved using 1D Tri-Diagonal Matrix Algorithm (TDMA) approach in the Matlab environment.

3. Results and discussion

Figs. 2 and 3 show the comparison between modeling results and experimental observations for a VRLA battery during cranking and charging processes with two different electric loads in the engine stop phase. The profile includes the following stages as indicated in figures:

1. With the engine on, the battery is being charged normally;
2. A “stop start” event occurs – the engine is turned off and the vehicle electric loads start to drain the battery;
3. The battery provides a large cranking current to crank the engine;

Table 3
Battery specifications.

Capacity (Ah)	65
Number of cells in series	6
Number of cells in parallel	8
Width of electrode plate (cm)	14.6
Height of electrode plate (cm)	13
Thickness of PbO_2 electrode (cm)	0.18
Thickness of separator (cm)	0.20
Thickness of Pb electrode (cm)	0.15
Porosity of PbO_2 electrode at fully-charged state	0.6
Porosity of separator	0.92
Porosity of Pb electrode at fully-charged state	0.6
Specific interfacial area of PbO_2 electrode ($\text{cm}^2 \text{cm}^{-3}$)	4e5
Specific interfacial area of Pb electrode ($\text{cm}^2 \text{cm}^{-3}$)	4e4
Concentration of acid (H_2SO_4) at fully charged state (mol cm^{-3})	5.36e-3
Operating temperature ($^\circ\text{K}$)	298

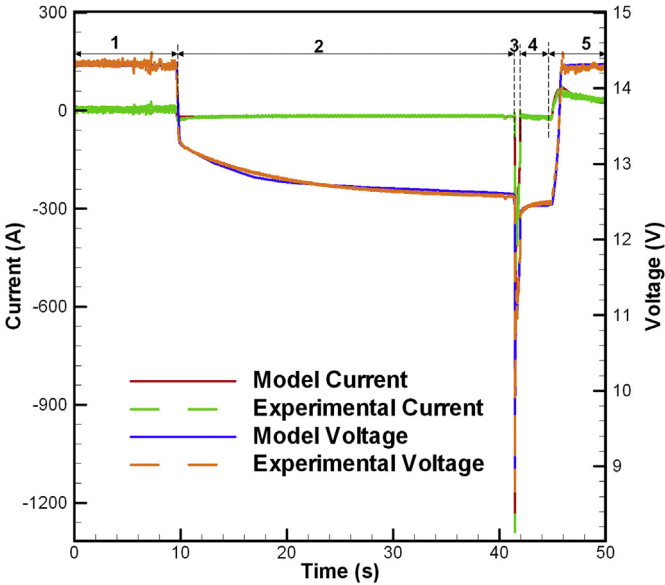


Fig. 2. Validation when electric load is low.

4. After the cranking pulse, the battery continues to support the vehicle electric loads when the engine speed is low;
5. When the engine speed increases, the alternator starts to charge the battery normally again.

From the figures above, it can be seen that the modeling results show good agreement with experimental observations. The experimental current (green line) and voltage (orange line) are mostly overlapped by modeling current (red line) and voltage (blue line), respectively. The predictions captured the transients of current and voltage behaviors during both cranking and charging processes. In Fig. 2, the vehicle electric load is low assumed at 20 A; Fig. 3 simulated a higher electric load during engine stop assumed to be 44 A. All the simulations in the following sections were conducted under the second stop–start cycle.

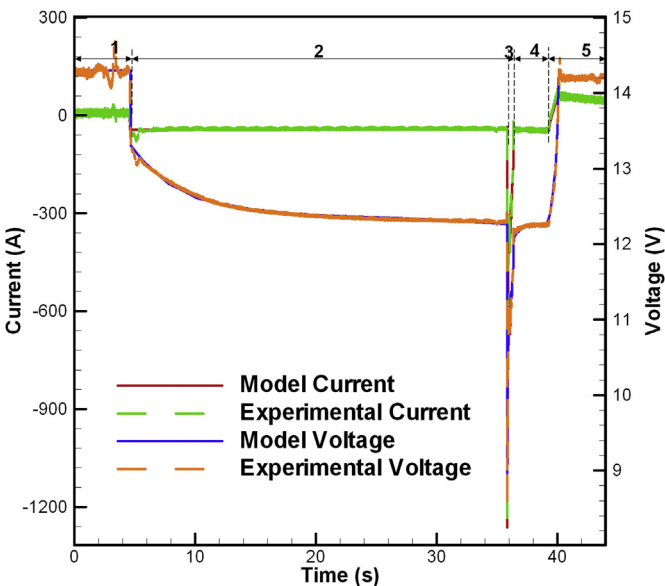


Fig. 3. Validation when electric load is high.

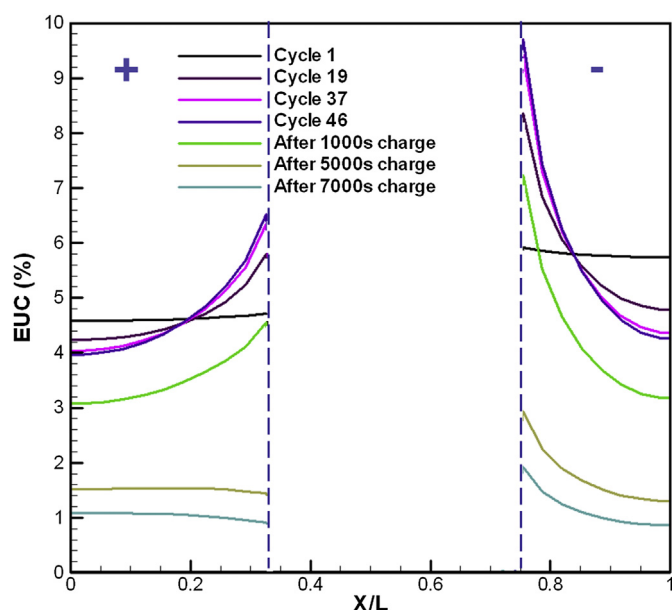


Fig. 4. Electrode utilization coefficient (EUC) distributions across the cell during stop-start cycling and follow-up charging.

3.1. Consistency of results with previous tear-down analysis

Electrode utilization coefficient (EUC) is defined as the percentage of loaded active material that has been consumed. In Fig. 4, the horizontal axis is the dimensionless length across the cell and the vertical axis is EUC. '+' represents the positive electrode and '-' represents the negative electrode. The battery started stop-start cycling at an initial SOC of 85%, and then was charged at a voltage of 14.3 V after cycling. From this figure, it can be seen that the consumption of active material at the positive electrode is lower than that of the negative electrode. This is because under such transient cycling, the double layer effect shares a significant part of the total discharge current. The positive electrode has a higher surface area and larger capacitance, such that the part of current from electrochemical reaction at the positive electrode is smaller than that of the negative electrode, which results in lower usage of the active material. Also, EUC distribution across the electrodes with cycling, especially in the negative side is non-uniform. This is due to the fact that the reaction at the interface between the separator and electrodes is more intense.

The cycling simulation has been done over 46 cycles, but the distribution of EUC across the cell after 46 cycles remained almost the same, which is due to that the initial effect of acid concentration uniform distribution in the electrodes starting from rest fades away. When the acid concentration gradient distribution gradually reaches steady state over cycling, the EUC distribution will stabilize accordingly because the distributions of open circuit voltage (OCV) and current density in the electrodes are strong functions of local acid concentration. Therefore the battery can be considered to have reached steady state of the EUC distribution after the 46th cycle and thus only the EUC distribution before the 46th cycle is shown here. It is also noted that the non-uniformity of EUC distribution in the negative electrode remained even after extended charging (5000–7000 s) under 14.3 V, while the non-uniformity in the positive electrode already disappeared. This is due to the fact that in this model double layer capacitance in the negative electrode is much lower than that in the positive electrode. During cycling more current goes into primary electrochemical reactions other than double layer effect in the negative electrode and thus higher and

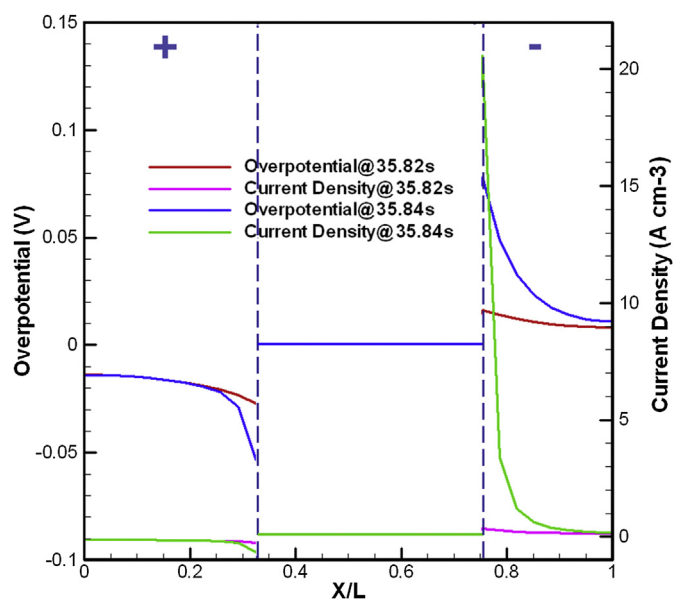


Fig. 5. Illustration of non-uniform distributions of current density and overpotential before and during a cranking process.

steeper EUC distribution has been formed. This leads to excessive charging time needed to fully charge the negative electrode. In other words, if the constant voltage charging continues for a sufficiently long period, the uneven distribution EUC in the negative electrode may be converted back, except this is unacceptable in practice. This result indicates that the sulfate produced at the interface between the separator and the negative electrode is converted back more slowly than any other locations at the negative side, while the reaction product can be evenly converted back at the positive side. According to the re-crystallization mechanism proposed in Refs. [4,5], small sulfate particles can re-crystallize into larger particles with flatter surfaces during the standing time, which are recognized as "hard sulfation". Therefore, the higher percentage of sulfate at the negative interface, either during cycling or after charging, may lead to more hard sulfation. Moreover, according to the quick-precipitation aging process proposed by Lam et al., at the locations of electrodes (near interface between the separator and the negative electrode) with higher current densities, the concentration of Pb^{2+} is higher and the ions precipitate more quickly, such that a compact and dense sulfate layer will be formed and it will stay after charging.

Fig. 5 explains the non-uniformity of reaction current across the cell via the overpotential. The plots at $t = 35.82$ s show the distribution of current and potential before the cranking pulse, and those at $t = 35.84$ s show the case during the cranking pulse. It can be seen in both cases that the overpotentials and current density at the interfaces between the electrode and separator are higher than any other locations in the electrodes. During cranking, the reaction at the interfaces between the separator and electrodes becomes more intense than before, especially at the negative side, while the current density at the end of electrodes almost remains the same as before. The cranking pulse draws high current from the negative interface near the separator very quickly, thus according to the quick precipitation aging mechanism that high-rate discharge leads to quick precipitation of Pb^{2+} that forms compact sulfate layer, or hard sulfation, the sulfate production at the negative interface may have a significant percentage that is dense and hard to recover.

Therefore, assuming the two aging mechanisms described in Refs. [1,4] are valid, the modeling results shown above predicted a

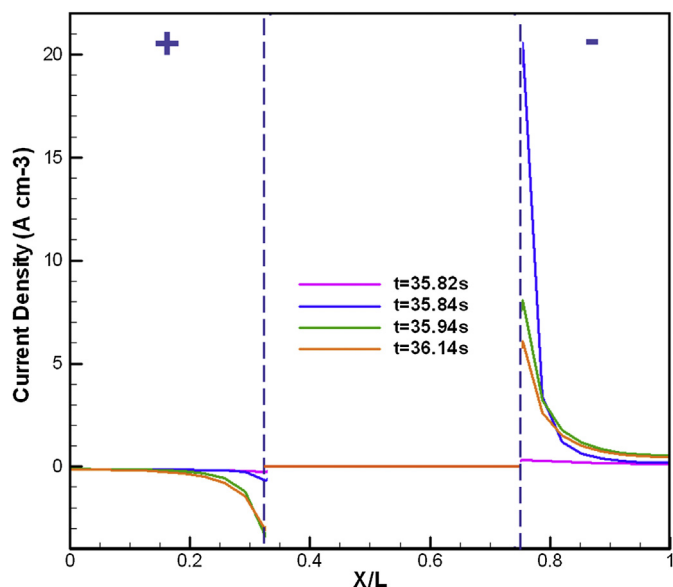


Fig. 6. Current density distribution during a cranking process ($t = 35.82$ s: prior to cranking; $t = 35.84$ s: start of cranking).

large potential such that the sulfate formed at the negative interface is more difficult to convert back and more likely to be left uncharged. This conclusion is consistent with the experimental observations in Lam's teardown study.

3.2. The effect of cranking

Fig. 6 shows the details of current density distribution across the cell at different time instant of the cranking process. It can be seen that during the cranking instant the current density increases more dramatically at the interface between the separator and negative electrode than anywhere else, and with the cranking current decreasing over time, the interfacial current density decreases

accordingly. It can be concluded that for the negative electrode, most of the current increment during a cranking process is contributed by the reactions occurring at the interface close to the separator, which verifies Lam et al.'s deductions from his experimental observations, that most of the Pb^{2+} ions precipitated at locations where high concentration of acid occurs in a high-rate discharge. The positive electrode, however, has a different situation. Due to the higher surface area and DL capacitance most of the current increment comes from DL current other than the electrochemical reaction during cranking, such that at the very instant of cranking $t = 35.84$ s the reaction current density is lower, and with the DL current decreasing over time the reaction current takes over. The fact that a lower peak current density occurs at the positive interface close to separator and thus the Pb^{2+} ions precipitate slowly may explain why the sulfate in the positive electrode was able to be fully recovered as observed in Lam's teardown analysis.

To show the effect of the cranking pulse on EUC over stop–start cycling, a modified cycling profile is composed as shown in Fig. 7b, which has the same discharge and charge Ah as the stop–start profile, but without a cranking pulse. The EUC after 46 cycles without cranking pulses is compared to those with cranking pulses. Again, more cycles have been simulated and the EUC barely changes after 46 cycles. Fig. 8 shows the EUC distributions through 46 no-cranking cycles, where it can be seen that the battery reaches steady EUC distribution after 46 cycles. The EUC distribution also shows peaks at the interfaces between electrodes and separator, which is due to the overpotential distribution pattern as explained before. Fig. 9 compares the steady EUC distributions under three cases: with cranking-pulse cycling, lower cranking-current (300 A) cycling and without cranking-pulse cycling. It can be clearly seen that the cranking process leads to a higher non-uniformity of EUC distribution across electrodes, especially in the negative electrode. Once again, this final steady distribution of EUC also verifies the explanation Lam et al. presented that Pb^{2+} ions tend to precipitate more at locations with higher acid concentration while less sulfate is produced at the locations far away from acid reservoir in high-rate discharge processes. The cranking pulse is apparently responsible for the increment of sulfate production at the negative

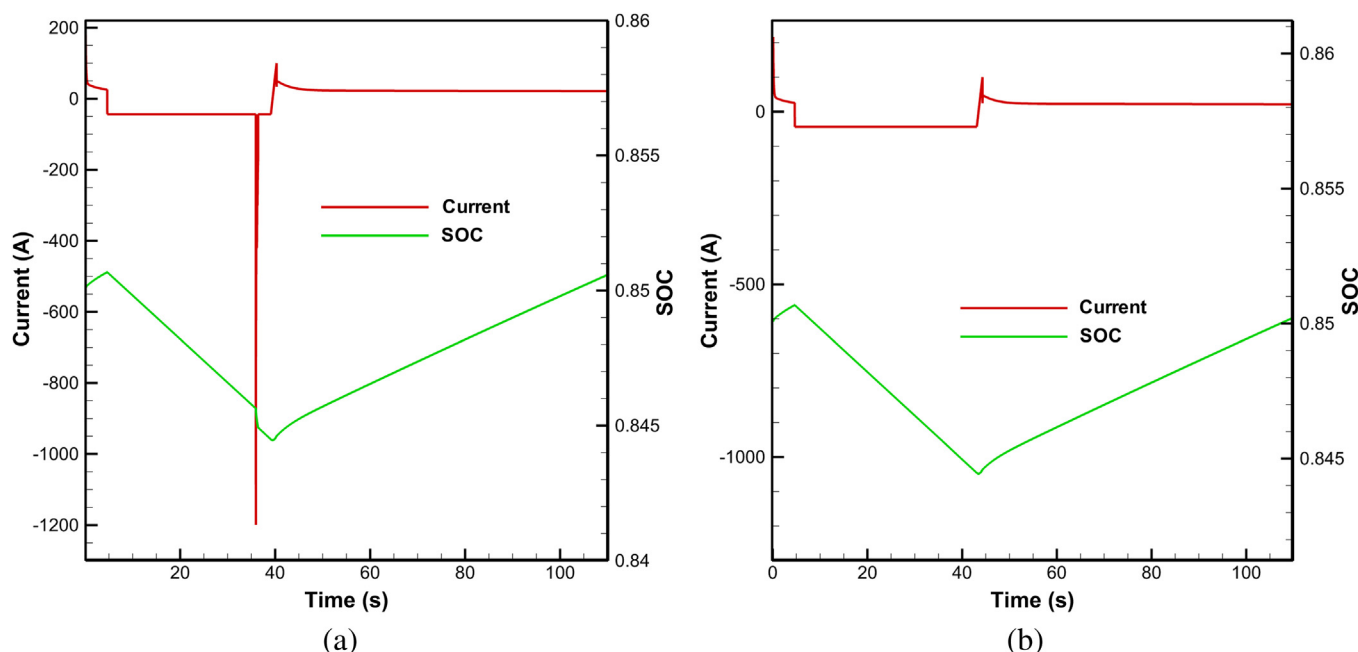


Fig. 7. New input cycling profile composed for comparison: (a) stop start cycle; (b) modified cycle.

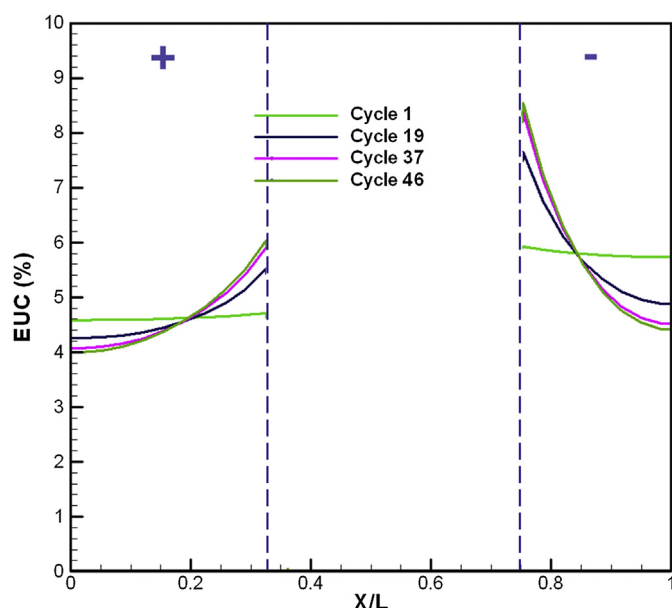


Fig. 8. EUC distribution evolution with cycling.

electrode interface close to the separator and the decrease at the end of the electrode. Based on the quick-precipitation aging mechanism, the increment at the negative electrode interface near separator due to the cranking pulses represents the sulfate with dense structure, and thus Fig. 8 also gives an estimate of how much “compact-layer” sulfate would be produced due to the cranking pulse over cycling. Also, the higher sulfate production at the negative electrode interface close to separator actually facilitates the re-crystallization aging at these locations. All in all, the predictions from both aging analyses would agree with the teardown observations of the negative surface sulfate layer after HRPSoC cycling in Ref. [1]. It is indicated from this figure that lowering the cranking current to 300 A doesn’t make much difference in terms of reducing interfacial sulfate production.

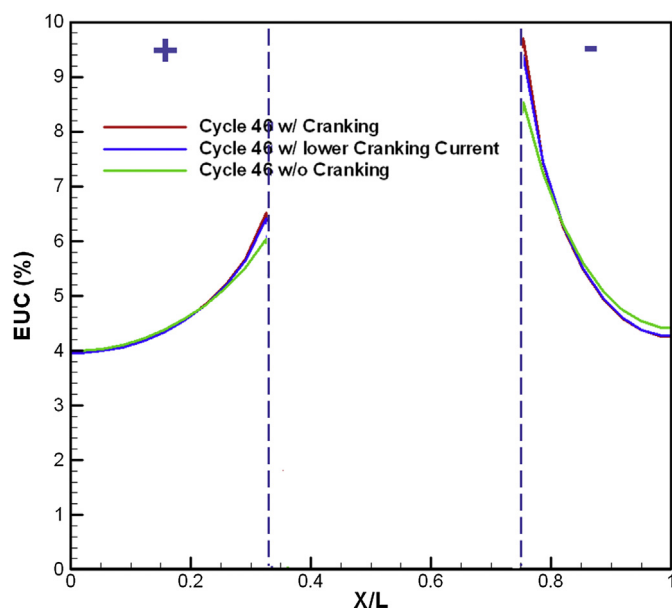


Fig. 9. EUC comparisons after 46 cycles with or without a cranking process.

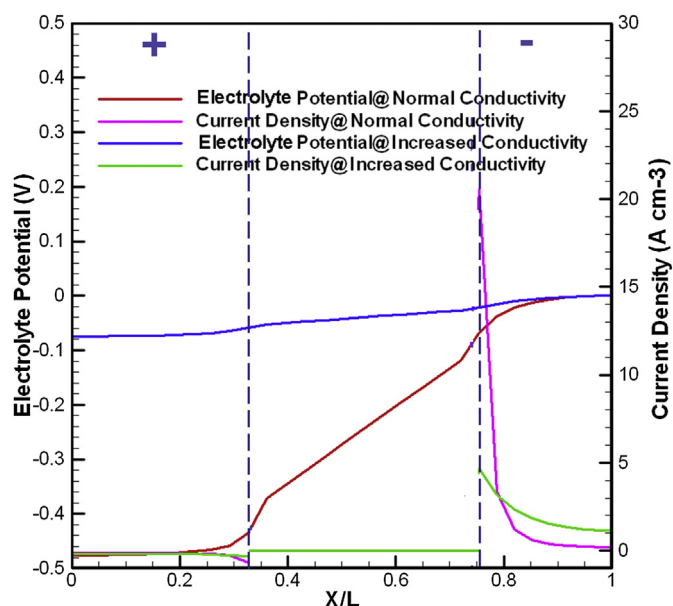


Fig. 10. The effect of increased electrolyte conductivity on potential and current density.

3.3. Further modeling results

This section is to study the effects of some critical cell design parameters on the distributions of current density and EUC during stop–start cycling and further analyze their impacts on battery cycle life.

3.3.1. Electrolyte conductivity

The solid phase potentials of the electrodes are uniform due to their large conductivities, thus the electrolyte potential distribution determines the non-uniformity of overpotential and current density, especially with a large cranking current being drawn. The electrolyte potential gradient from one electrode to the other mainly depends on the electrolyte conductivity. In order to show the significance, Fig. 10 shows the simulation results of the potential and current density distributions during the cranking pulse if the electrolyte conductivity were increased by a factor of 10. It can be seen that the peak of current density at the negative electrode interface near the separator during the cranking process is significantly reduced, which means the intensified Pb^{2+} precipitation during the high-rate discharge instant is greatly relieved, thus the formation of the compact sulfate layer with dense structure can be prevented and the battery life can be extended. The electrolyte conductivity could be increased by using chemical additives.

3.3.2. Specific surface area

When it comes to porous electrodes, the specific surface area, defined as the active surface area per unit volume ($\text{cm}^2 \text{cm}^{-3}$) is always an important design parameter that greatly impacts the performance and longevity of a battery. The effects of specific surface area of both electrodes are studied in this section.

Figs. 11 and 12 display the current density distributions across the cell both from electrochemical reactions and double layer effect, before and during a cranking event. In Fig. 11, the battery has reached steady state before cranking, thus the DL current is 0 and all the current is drawn from the electrochemical reaction. A higher surface area of the negative electrode leads to higher peak of current density at the interface close to the separator. This is due to the non-linear distribution of overpotential and current density across

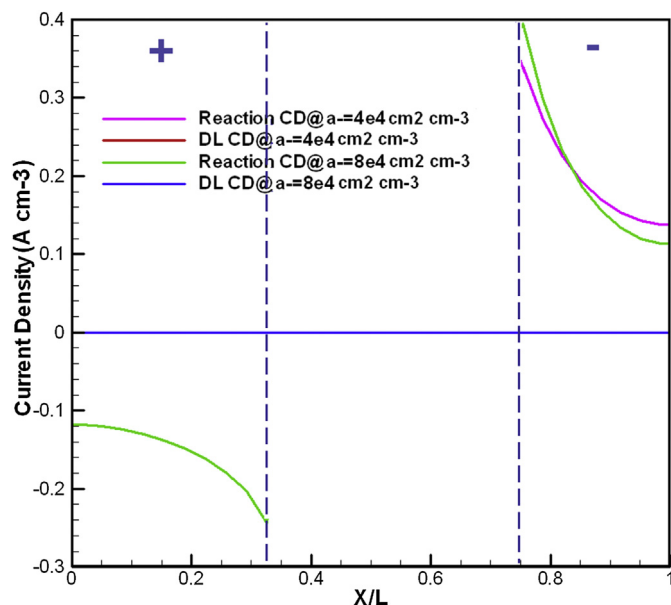


Fig. 11. Distributions of reaction and double layer (DL) current density (CD) before cranking.

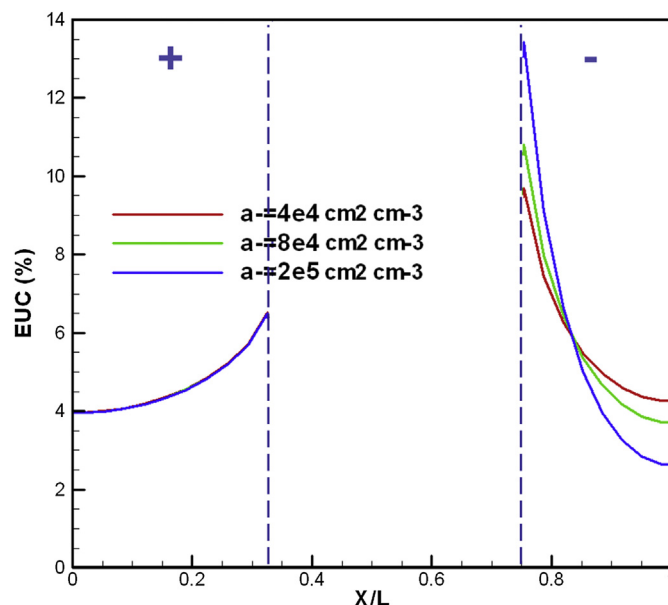


Fig. 13. The effect of negative surface area on EUC distribution across the cell after 46 cycles.

the negative electrode. When the surface area increases, the over-potential and current density distribution adjust themselves as the total current into the negative electrode is a constant. The numerical solution indicates that increasing negative electrode surface area causes more current drawn from the interface between the negative and separator. In Fig. 12, the same simulation is run when the cranking current is being drawn. Now the double layer current plays a role due to the large electrode potential change. This figure shows that a higher surface area in the negative electrode has a larger double layer capacitance, such that during the transient cranking process more DL current takes part of the whole cranking current, which relieves high demand of reaction current at the interface between the electrode and separator. This is desirable and

beneficial because the intensified reaction at the interface under large cranking current can be prevented by increasing the surface area, which consequently leads to less dense sulfate production at the interface.

Fig. 13 shows the EUC distribution across the cell after 46 cycles, which means that the battery has reached the steady state of EUC distribution. It can be seen that a higher negative electrode surface area leads to more non-uniform EUC distribution that has a higher peak of sulfate remaining at the interface near separator during the cycling. This is because most of the active material is converted to sulfate in the stop-discharge phase of each cycle other than the cranking pulse, which means the distribution of EUC is determined by current density during the stop-discharge phase. A higher percentage of sulfate remaining during cycling may cause more particles re-crystallized into hard sulfation and thus capacity loss.

To conclude, on one hand, the increase of surface area in the negative electrode results in a more non-uniform distribution of remaining sulfate during cycling and may lead to more hard sulfation at the interface near the separator; On the other hand, a higher surface area can effectively increase the double layer capacitance that relieves the high peak of current drawn from the interfacial locations close to the separator, which can prevent the quick precipitation of Pb^{2+} and avoid producing dense sulfate layers. In practice, the trade-offs between these two effects have to be made based on the operation profile, such as the frequencies of stop and start, of batteries.

A similar study is conducted on the positive electrode. Fig. 14 shows the effect of specific surface area of the positive electrode on final steady EUC-after 46 cycles. The same conclusions can be reached as for the negative electrode. A higher surface area leads to higher remaining sulfate at the interface near the separator during cycling. However, the positive electrode does not have the same high peak current density as the negative during the cranking due to the higher double layer capacitance as shown earlier in Fig. 6. The ion precipitation and sulfate formation at the positive side is not as intense as those at the negative interface near the separator during cranking, which makes it easier to recover sulfate in the positive electrode. Therefore, for the positive electrode the re-crystallization aging mechanism should be the only concern and increasing the

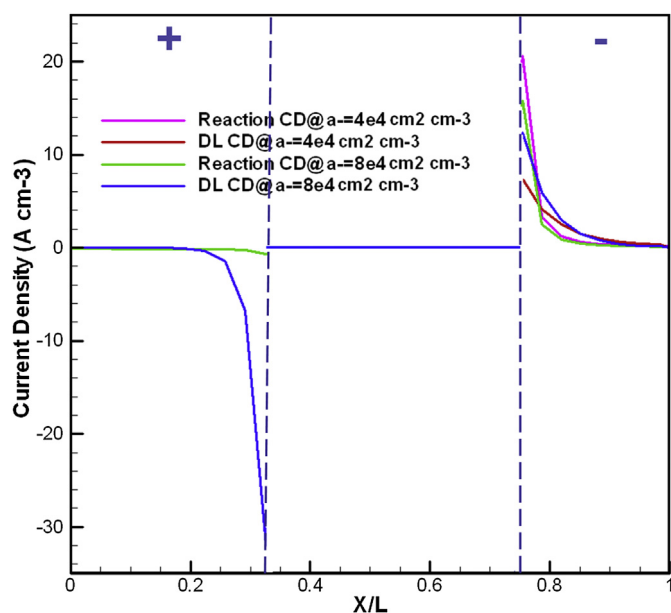


Fig. 12. Distributions of reaction and double layer (DL) current density (CD) during cranking.

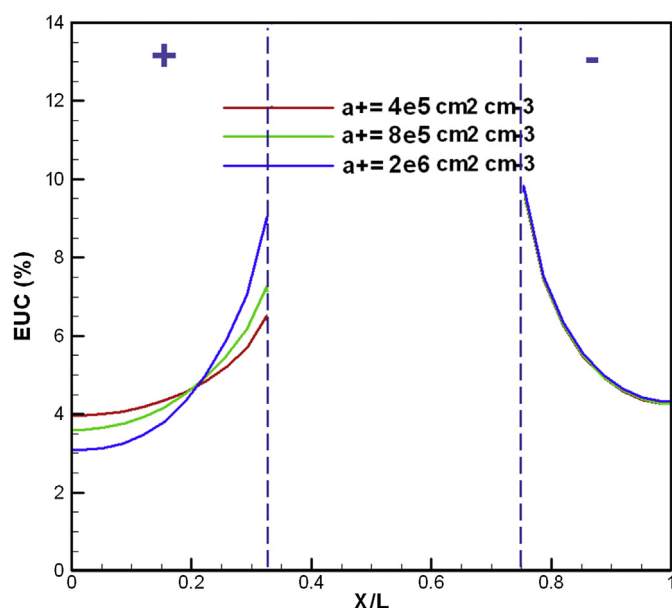


Fig. 14. The effect of positive surface area on EUC distribution across the cell after 46 cycles.

specific surface area may prevent hard sulfation produced at the locations close to the separator.

3.3.3. Capacitance

Since the capacitance of the positive electrode is usually larger than that of the negative, which effectively protects the positive from discharging at a high peak of reaction current during a cranking pulse. The transient quick ion-precipitation aging mechanism impacts the negative electrode more than the positive electrode. Therefore only the effect of double layer capacitance of the negative electrode on aging caused by the high-rate discharge–cranking process is studied in this section.

Fig. 15 shows the effect of double layer capacitance (C_{dl}) in the negative electrode on the distribution of current density across the

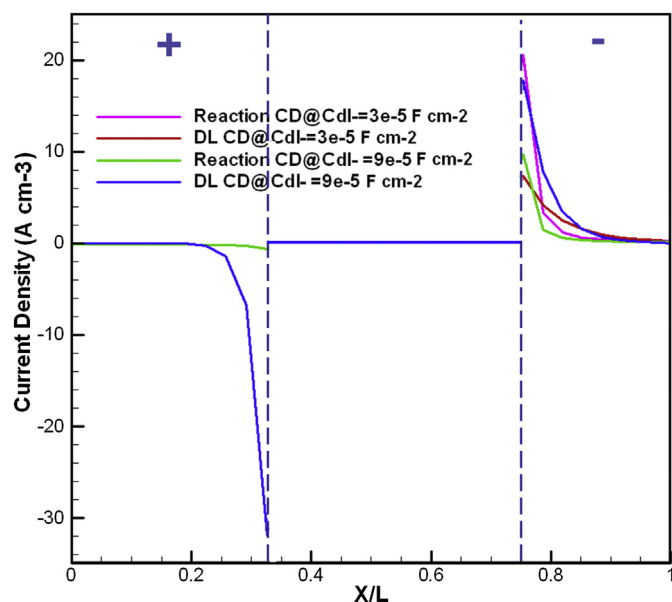


Fig. 15. The effect of C_{dl} (double layer capacitance) in the negative electrode on the distribution of current density across the cell.

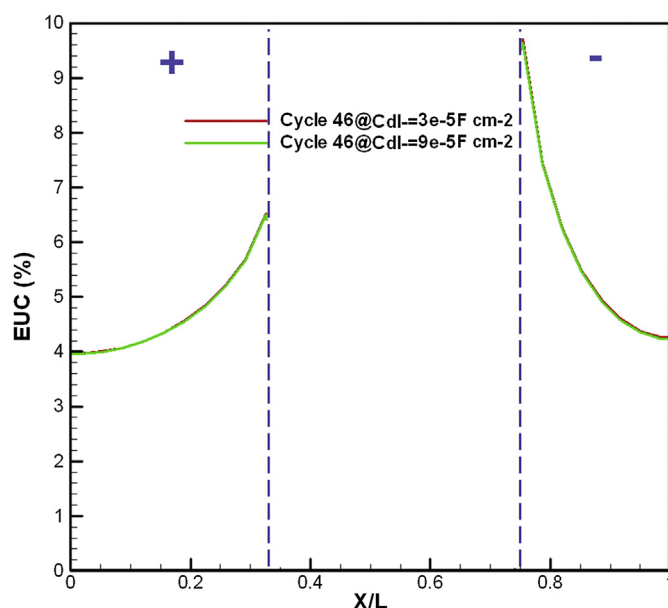


Fig. 16. The effect of double layer capacitance in the negative electrode on the distribution of EUC after 46 cycles (red and green lines overlap). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

cell. It can be seen that with an increase of capacitance from $3e-5 \text{ F cm}^{-2}$ to $9e-5 \text{ F cm}^{-2}$, the DL current density increases significantly, and the reaction current peak at the interface is reduced from over 20 A cm^{-3} to below 10 A cm^{-3} , which greatly lowers the possibility of forming a dense sulfate layer and capacity loss.

Fig. 16 gives the effect of double layer capacitance in the negative electrode on the distribution of EUC after 46 cycles. Once again, due to the small fraction of cranking pulse in the entire stop–start profile in terms of active material consumption the capacitance and the transient current density distribution barely affect the steady EUC distribution during cycling. This means the hard sulfation aging due to the re-crystallization of standing sulfate is not influenced by the change of negative capacitance. From these two figures, it can be concluded that an increase of the negative electrode capacitance benefits more in preventing the dense sulfate layer formation in a high-rate discharge than the re-crystallization of sulfate particles during the stop–start cycling.

4. Conclusion

The cranking and charging processes of a conventional valve-regulated lead-acid battery without carbon additive or carbon-impregnated electrodes in a stop–start cycle were simulated by using a mathematical model to study the formation and distribution of lead sulfate across the cell. The resulting effects on battery aging over cycling based on two aging mechanisms were analyzed. The simulation results showed consistency with the teardown observations and analyses in a previous study, predicting a large potential that the sulfate formed at the negative interface is more difficult to convert back and more likely to be left uncharged. The results indicated that for the negative electrode, most of the current increment during a cranking process was contributed by the reactions occurring at the interface close to the separator, which led to more dense sulfate layers produced therein. Also, the electrode utilization coefficient distribution comparison to cycling without cranking pulses gave a quantitative estimate of compact layer produced at the negative interface near the separator due to the cranking process. Parametric studies showed higher electrolyte

conductivity led to a lower peak of current density at the negative electrode interface during the cranking process which could relieve the intense sulfate layer production. Increasing the specific area and double layer capacitance of negative electrode both effectively reduced the peak of current density and dense sulfate layer production at the interface between the negative and separator, but a higher surface area also resulted in a more non-uniform electrode utilization coefficient distribution over cycling, indicating a higher percentage of sulfate re-crystallization at the interface. The simulation results and analyses based on two aging mechanisms provide insights into the underlying physics and guideline for designing lead acid batteries for micro-hybrid applications.

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